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Field procedures and results of groundwater sampling in kimberlite from drillholes in the Kirkland Lake and Lake Timiskaming areas, northeastern Ontario[1]

J.A. Sader, M.I. Leybourne, M.B. McClenaghan, S.M. Hamilton, and K. Robertson

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Abstract: A hydrogeochemistry study of the Lake Timiskaming and Kirkland Lake kimberlite fields was undertaken as part of the Geological Survey of Canada's Targeted Geoscience Initiative (TGI). The goals are to understand the hydrogeology and geochemistry of groundwater in kimberlite compared with the surrounding Archean rocks and to develop a useful kimberlite exploration tool. Groundwater in holes drilled by exploration companies in the 1980s was sampled at five kimberlite pipes: B30, C14, A4, Diamond Lake, and 95-2. The water was measured in the field for pH, oxidation-reduction potential (Eh), dissolved oxygen, electrical conductivity, and temperature. Preliminary field results indicate that many pH values are unusually high for natural groundwater, with pH levels in B30, C14, and A4 as high as 11.00 to 12.45. Field analyses and pump-recovery tests reveal that a link may exist between the hydration of olivine and the production of CH_4 and H_2 and groundwater flow.

Résumé : Dans le cadre de l'Initiative géoscientifique ciblée (IGC) de la Commission géologique du Canada, on a entrepris l'étude hydrogéochimique des champs de kimberlites du lac Témiscamingue et de Kirkland Lake. L'objectif de l'étude est de comprendre l'hydrogéologie et la géochimie de l'eau souterraine qui circule dans les kimberlites par rapport à celle qui est présente dans les roches encaissantes de l'Archéen, afin de mettre au point un outil d'exploration efficace des kimberlites. Des échantillons d'eau ont été prélevés dans les trous que diverses sociétés d'exploration ont forés au cours des années 1980 dans les cinq kimberlites suivantes : B30, C14, A4, Diamond Lake et 95-2. On a mesuré sur le terrain le pH, le potentiel d'oxydo-réduction (Eh), la teneur en oxygène dissous, la conductivité électrique et la température des échantillons d'eau. Les résultats provisoires des travaux sur le terrain indiquent que le pH d'un grand nombre d'échantillons est inhabituellement élevé pour une eau souterraine naturelle; le pH de l'eau provenant des kimberlites B30, C14 et A4 atteint entre 11,00 et 12,45. Les analyses sur le terrain et les essais effectués à l'aide de pompes démontrent qu'il y a peut-être un lien entre l'hydratation de l'olivine, et la formation concomitante de CH_4 et de H_2, et l'écoulement de l'eau souterraine.

[1] Contribution to the Targeted Geoscience Initiative (TGI) 2000–2003.

INTRODUCTION

The first reported discovery of kimberlite in northeastern Ontario was by Satterly (1949). Since the 1980s, numerous kimberlite pipes and dykes have been discovered in the Kirkland Lake and Lake Timiskaming areas through the use of geophysical and indicator-mineral methods (Brummer et al., 1992a). Groundwater analysis, however, has never been used in this area as an exploration tool for kimberlite. To our knowledge, only one other study has investigated the chemistry of groundwater associated with kimberlite (Kosolapova and Kosolapov, 1962).

Water was sampled from diamond- and rotary-drill holes in five kimberlite pipes in the Kirkland Lake and Lake Timiskaming areas (Fig. 1). These samples will undergo analysis for major- and trace-element concentrations and various stable (O, H, C, S) and radiogenic (Pb, Sr, Nd) isotopes. Initial field data collected include the pH, oxidation-reduction

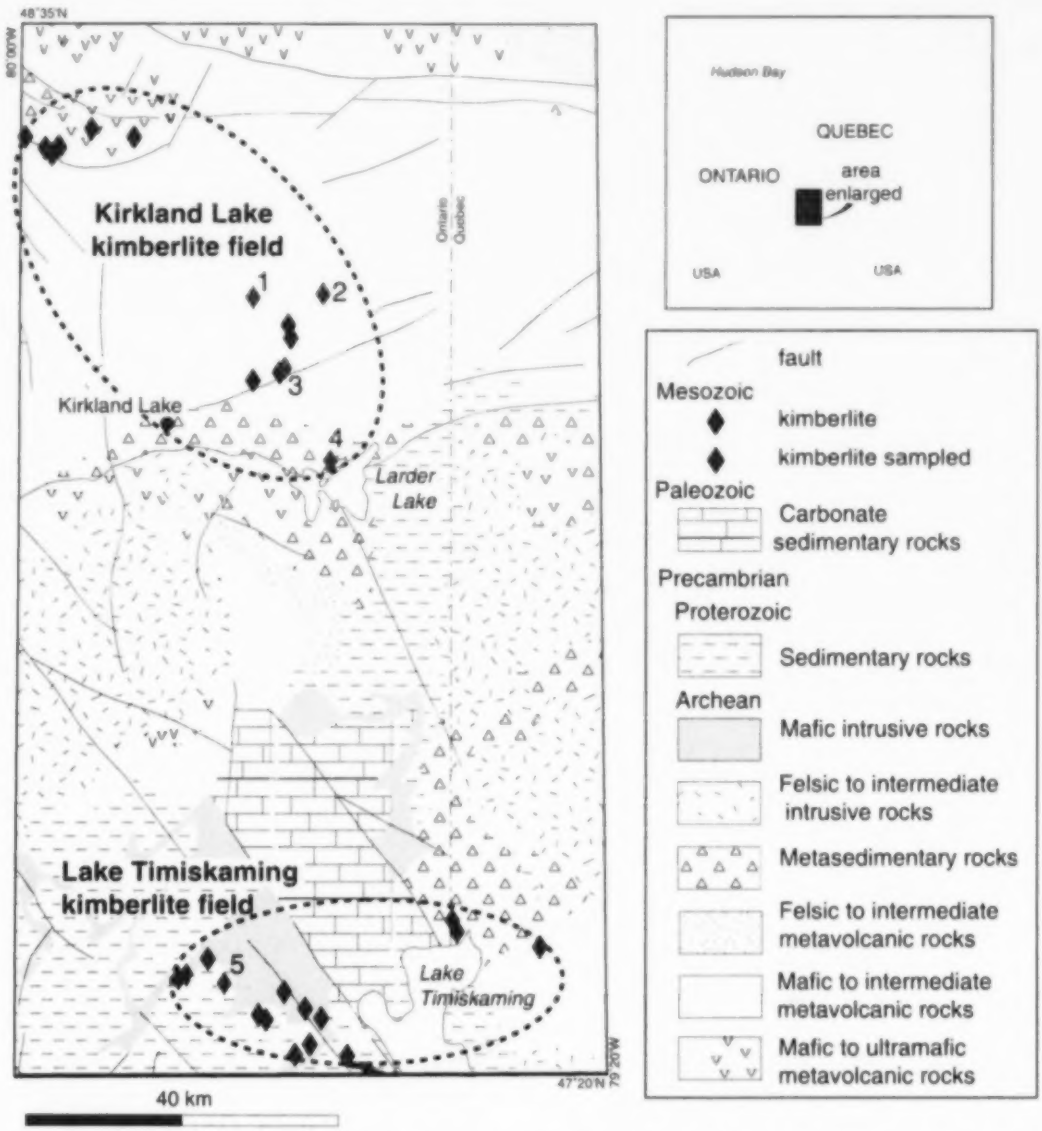


Figure 1. *Location of the Kirkland Lake and Lake Timiskaming kimberlite fields in northeastern Ontario and the five kimberlite pipes sampled in this study (1, B30; 2, C14; 3, A4; 4, Diamond Lake; 5, 95-2). Bedrock geology modified from Ontario Geological Survey (1991).*

potential (Eh), dissolved oxygen, electrical conductivity, and temperature of the water. These initial data are very promising and set the stage for further analyses of kimberlitic water.

KIMBERLITE GEOLOGY

Four of the five kimberlite pipes sampled (A4, B30, C14, and Diamond Lake) are within the Kirkland Lake kimberlite field. The geological context in which they occur is very similar and the pipes are all approximately the same age (155–160 Ma). The host rocks are Archean mafic to felsic volcanic rocks and felsic to intermediate intrusive rocks, intruded by Proterozoic mafic dykes (Jensen, 1975). At the time of kimberlite emplacement, the area was overlain by Paleozoic carbonate rocks (Brummer et al., 1992b) estimated to have once been 700 m thick (Armstrong and McCracken, 1996). Although the Paleozoic sedimentary cover has been removed by preglacial weathering and glacial erosion, fragments of limestone up to 1 m in diameter can be seen in the diatreme facies of the kimberlite (McClenaghan et al., 1999b). Limestone is visible in the diatreme facies because of a process called 'drawdown', by which these xenoliths appear in the kimberlite facies below the rocks originally intruded by the kimberlite (Mitchell, 1986). The fifth kimberlite, 95-2, is in the Lake Timiskaming kimberlite field, 80 km south of Kirkland Lake. Unconsolidated glacial sediments of varied porosity and permeability overlie the kimberlite bodies. Between 20 and 50 m of sand, silt, clay, and till were deposited on top of the pipes during glaciation of the region at 9000 ka.

A4

The A4 kimberlite, also known as the 'Alfie Creek 1 pipe', is in Arnold Township at UTM co-ordinates (NAD 27) 0583142 E and 5341294 N in UTM Zone 17; it is close to the North Arm of Victoria Lake (Fig. 2). The elevation taken from a 1:20 000 scale topographic map is 315 m above sea level (a.s.l.). Monopros Ltd. discovered this pipe in 1983 and Lac Minerals Ltd. completed additional drilling on the kimberlite in 1987.

During the approximately 156 Ma since kimberlite emplacement, the Paleozoic carbonate rocks, the crater facies kimberlite, and part of the diatreme facies have been removed by erosion, leaving a subcropping diatreme facies (McClenaghan et al., 1999a) under 45 to 55 m of glacial sediments. The kimberlite has been preferentially weathered to produce a bedrock depression, typical of kimberlite in this region. This depression has been filled by glacial sediments, mainly till and glaciolacustrine sediments. The kimberlite contains 10 to 14% clasts that are up to 4 mm in diameter and consist of limestone and calcareous mudstone, minor volcanic rock, and ultramafic nodules (Brummer et al., 1992a), as well as abundant macrocrysts of olivine, garnet, ilmenite, and phlogopite (Brummer et al., 1992a). Xenoliths of Archean metavolcanic and Paleozoic carbonate rocks are present and vary from <1 to 4 cm in diameter (McClenaghan et al., 1999a).

B30

The B30 pipe, also known as the 'Nickila Lake pipe', is in Bisley Township at UTM 0580322 E and 5348175 N in UTM Zone 17; it is close to Esker Lakes Provincial Park (Fig. 2). The surface elevation taken from a 1:20 000 scale topographic map is 326 m a.s.l. and the approximate dimensions are 200 m by 400 m. The pipe is located beneath a small depression filled by Nickila Lake and has been dated at 157 Ma (Brummer et al. 1992a). Both Monopros Ltd. and Lac Minerals Ltd. have carried out drilling at B30. Hole 85-06-02 is a rotary/percussion-drill hole drilled by Monopros Ltd. in 1985. It was blocked at approximately 30 m, which coincides with the contact between the overburden and weathered kimberlite. Sage (1996) and McClenaghan et al. (1996) noted that the B30 kimberlite was much softer and friable than the other kimberlite bodies sampled in the Kirkland Lake area. Drill core obtained from Lac Minerals Ltd. and analyzed by Brummer et al. (1992b) is described as lithic-tuffisitic breccia to pelletal-tuffisitic breccia containing 10 to 20% xenolithic material. Sage (1996) analyzed the drill core obtained from Monopros Ltd. and found angular Paleozoic limestone clasts up to 2 to 3 cm in diameter. He also found traces of ilmenite and serpentinized olivine megacrysts 4 to 5 mm in diameter. Other nodules, such as nodules of ultramafic granulite, glimmerite, peridotite, and rare eclogite as well as deformed pelletal lapilli 1 to 10 cm in diameter, are abundant (Brummer et al., 1992b).

The surficial geology at the B30 pipe consists of a mix of glacial till and glaciofluvial sediments. A depression formed over the pipe has been filled with glacial sediment. Till thickness varies from approximately 30 m to 70 m over the kimberlite and is approximately 20 m over the Archean rocks (andesitic tuff to the north and pillowed andesite and dacite to the south) (Brummer et al., 1992b).

C14

The C14 kimberlite pipe is located in Clifford Township, at UTM 0588751 E and 5348074 N in UTM Zone 17 (Fig. 2). Its dimensions are approximately 200 m by 300 m (McClenaghan et al., 1999b). The surface elevation taken from a 1:20 000 scale topographic map is 315 m a.s.l. The land surface at C14 is swampy and slightly depressed. Many drillholes were sampled; most, however, were in the northwest and northcentral parts of the kimberlite (Fig. 2). The property has been explored by Lac Minerals, Dia Met Minerals, and Regal Goldfields, with drilling completed by all three companies. The pipe appears to be at a transition zone between diatreme and hypabyssal facies (Sage, 1996). Water samples have been collected from the different facies. The kimberlite is similar in composition to other kimberlite bodies in the Kirkland Lake area. It contains several different phases (tuffaceous kimberlite breccia, coarse tuffaceous breccia, hypabyssal kimberlite, and tuffaceous kimberlite; Brummer et al., 1992b), all of which contain clasts of Paleozoic rocks. The groundmass contains serpentine, phlogopite, chlorite, and calcite (McClenaghan et al., 1999b). The matrix is composed of a fine-grained mixture of

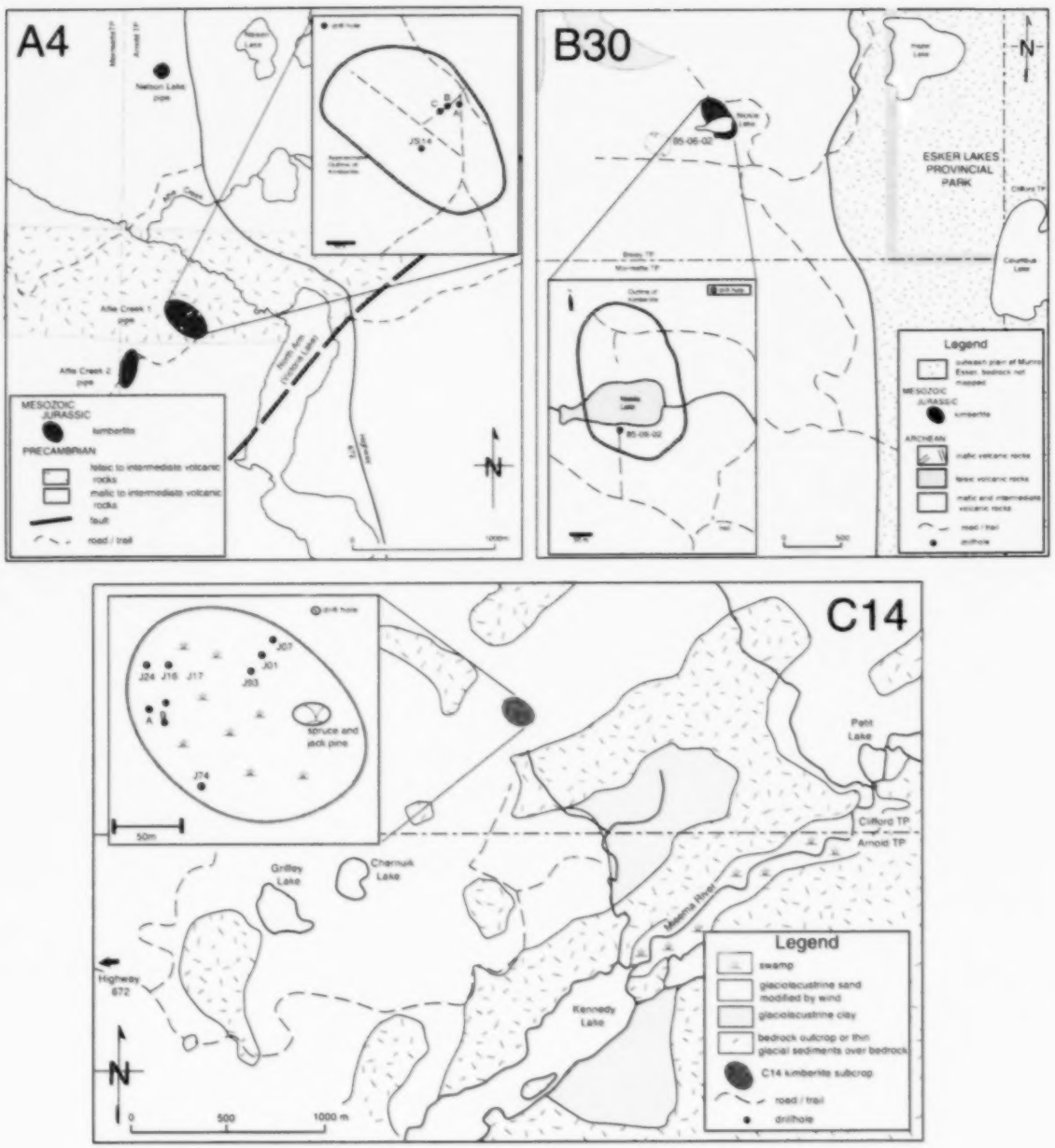


Figure 2. *Location of the A4, B30, and C14 kimberlite pipes and drillholes sampled in this study.*

carbonate, chlorite, and serpentine (Sage, 1996). The surrounding basement rocks are Archean dacite and a feldspar porphyry. The kimberlite is overlain by 7 m of silty sand till, 2 m of well sorted sand, and 23 m of glaciolacustrine clay and silt. At surface, eolian sand dunes overlie part of the kimberlite.

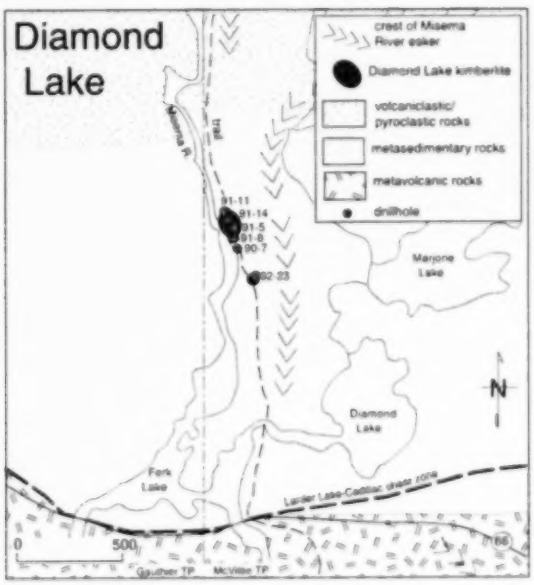
Diamond Lake

The Diamond Lake kimberlite, discovered by Sudbury Contact Mines Ltd. in 1989, is located on the west flank of the Misema River esker in McVittie Township. The UTM co-ordinates at its southernmost point are 0592450 E and 5329933 N (NAD27) in Zone 17 (Fig. 3). The elevation taken

from a 1:20 000 scale topographic map is 280 m a.s.l. The kimberlite measures 250 m by 100 m (McClenaghan et al., 1998). Diamond-drill hole 90-7 intersected a small, 15 m wide blow 300 m south of the large main pipe. Both of these bodies are thought to have been emplaced at the same time (McClenaghan et al., 1998) and have been intruded along the east flank of a north-trending diabase dyke (Sage, 1996). The kimberlite groundmass has a composition similar to that of kimberlite elsewhere in the Kirkland Lake region. Serpentine, phlogopite, chlorite, and calcite are the major minerals (McClenaghan et al., 1998). The diatreme facies contains 15 to 25% xenoliths and is a pelletal-textured kimberlite matrix. Below the diatreme zone, in the hypabyssal zone, the rock is fine to medium grained and is estimated to contain 50 to 75% olivine and smaller amounts of opaque minerals and minor garnet and phlogopite (Sage, 1996). The surrounding country rocks consist of Archean greywacke and conglomerate (McClenaghan et al., 1998). The kimberlite is overlain by glaciofluvial sand and gravel 60 to 80 m thick.

95-2

The 95-2 kimberlite pipe (Fig. 3) is located in Lundy Township at UTM co-ordinates 0583334 E and 5263598 N in UTM Zone 17 (NAD27), approximately 12 km west of the town of New Liskeard. The elevation taken from a 1:20 000 scale topographic map is 300 m a.s.l. The pipe measures approximately 220 m by 120 m and intruded Proterozoic (Huronian) siltstone. Although its age has not yet been determined, it is likely within the range of other known kimberlite pipes in the Lake Timiskaming field (134–154 Ma; Brummer et al., 1992b). Less erosion has occurred in this area and the 95-2



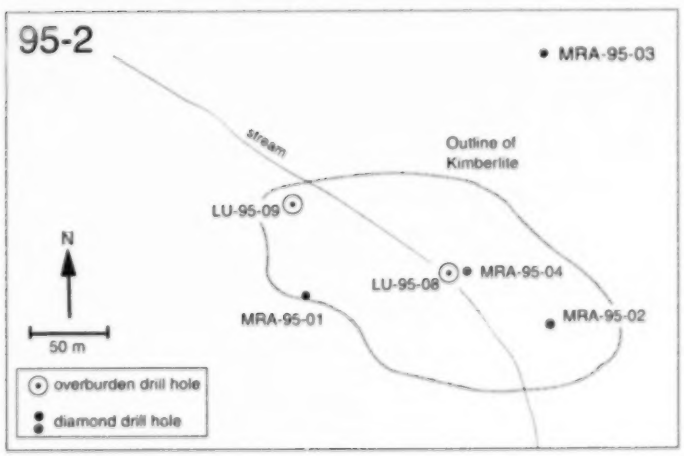


Figure 3.

Location of the Diamond Lake and 95-2 kimberlite pipes and drillholes sampled in this study.

pipe appears to be diatreme facies for all depths sampled. It is overlain by approximately 10 m of till, which in turn is overlain by 40 m of glaciofluvial sand and gravel.

FIELD AND ANALYTICAL METHODS

Sampling

For this study, groundwater samples were collected from exploration holes drilled into the kimberlite between 1983 and 1989. The pH, conductivity, oxidation-reduction potential, dissolved oxygen, and temperature of groundwater samples were measured in the field at the time of collection with a Quanta Multiprobe manufactured by Hydrolab Corporation®. However, temperature values are not accurate for sampling done with the packer or downhole pump because of the time required for the water sample to be pumped to the surface. Temperature values for samples collected with the Grundfos pump are accurate because the water is pumped out much faster and there is no extra tubing at ground surface through which the water must move and where the temperature could change.

The conductivity and pH of the pumped water were measured once the reading had stabilized. The oxidation-reduction potential was typically measured after the first, third, and fifth minutes. Dissolved oxygen was measured when the Quanta Microprobe displayed the lowest reading of this parameter. Because many slugs of sample must be removed before a sample is taken for laboratory analysis, stabilization of pH, electrical conductivity, and Eh are interpreted to represent flow specifically from the depth being investigated.

Nalgene sample bottles (high-density polypropylene or HDPE) of different sizes were used for most samples (filtered cation, filtered anion, and radiogenic isotope analyses). Polypropylene (PP) sample bottles were used for samples to be analyzed for O and H isotopes and were filled right to the top with no head space. Amber plastic or glass bottles were used for samples for $\delta^{13}C$ analysis and were also filled right to the top with no head space. All covers were hand tightened and sample bottles were refrigerated to prevent isotope fractionation. The sulphate and sulphide samples were collected in one-gallon HDPE jugs that were cleaned and reused daily.

A number of sampling devices were used, including a straddle-packer, a Grundfos pump, and a double-valve pump (top part of the packer). Two types of straddle-head packer systems were used, a sliding-head packer system built by the GSC that uses RST Instruments Ltd. packer heads, and a fixed-head packer built by Solinst Canada Ltd. However, only the sliding head packer could be worked for our purpose because of the rigidity and small amount of expansion of the fixed-head type. Fixed-head packers would be more useful where the drillholes are fairly recent and fully cased with screens.

Both types of packer work by inflating upper and lower sections of piping that is surrounded by rubber tubing. Between the two packers is a pipe approximately 1.5 m long that is perforated to allow groundwater through the upper packer into a sample chamber located immediately above the upper packer. The upper and lower packers are inflated using compressed N2 gas, sealing the zone with the perforated pipe in the middle. Numerous slugs of water are taken in order to flush the water column of the initial standing water. This gives a better indication and more accurate sampling of groundwater at a given depth. Nitrogen gas was used to force the water sample to the surface. Gas pressure was regulated using a regulator on the tank and a control box. A reel holding the tubing is held on a trolley that can be moved around on wheels. A larger, electrically operated reel was used at one hole to reach depths below 200 m. The hand reel system is limited to a depth of 145 m; another drawback of this system is that packer operation can be very problematic and the packer has many parts that can (and do) fail. However, the straddle-packer system produces the best depth-specific samples.

A double-valve pump manufactured by Solinst Canada Ltd. was also used in this study. In this method, the pump head was simply lowered to any given depth in the hole and N_2 gas was used to drive a column of water to the surface. On a number of occasions, the drill-hole diameter was either too large or too small for either packer system, and using the pump head was the only sampling method available. The drawback of using the double valve pump rather than the full packer is that the water sampled from any given depth may be mixed with water not specifically from that zone.

A third sampling method was used in this study. It involved using a Grundfos electric pump powered by a gasoline generator. The device was used to pump water up and out of the drillhole from a maximum depth of approximately 20 m and to carry out pump tests in holes at sites 95-2, C14, and A4. The drawback of this sampling procedure is that the water sampled may be mixed with water from other zones and thus not a true indication of the water flowing at that depth.

Geophysical logs

At selected holes, geophysical borehole data were used to constrain optimal locations for sampling groundwater from fracture zones. Drillhole A at pipe A4 was sampled at depths corresponding to geophysical logs obtained from J. Mwenifumbo (unpub. data, 1993) of the Geological Survey of Canada. The depths were chosen on the basis of density and temperature gradients.

Chemical treatment of water samples

Various chemicals were added to some of the water samples collected. Each sample set taken included a sample for sulphide and sulphate testing. Samples for sulphate testing were collected in a one-gallon jug. Sample size was typically 1 to 1.5 L. Excess barium chloride was added to each sample taken for sulphate testing; if sulphates are present, barium sulphate $BaSO_4$ (barite) will precipitate from solution (equation 1).

$$BaCl_2(s) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + Ci_2(aq) \quad (1)$$

Once the precipitate had settled to the bottom of the container, the sample was decanted and filtered through 0.45 µm filters (typically at the end of the same day the sample was collected). The filtrate was air dried and kept for $\delta^{34}S$ isotopic analysis if barite had precipitated from solution.

Zinc acetate ($ZnC_2H_3O_2$) was added to water samples to test for sulphides. One to two grams of zinc acetate were added to a 1 to 2 L water sample in a one-gallon HDPE jug. Care was taken not to shake the sample immediately after adding the zinc acetate so as to avoid oxidization of aqueous sulphide. A precipitate forms if sulphates are present; the reaction produces ZnS (sphalerite) (equation 2).

$$ZnAc(s) + HS^-(aq) \rightarrow ZnS(s) + H_2O(aq) + CO_2(g) \quad (2)$$

As with the sulphate sample, the sulphide precipitate (if any) was allowed to settle to the bottom, then the water was decanted off the top and filtered (usually at the end of the same day the sample was collected). Small amounts of mercuric chloride were added to the samples taken for $\delta^{13}C$ analysis to kill any bacteria that could fractionate the carbon isotopes.

FIELD BOREHOLE GEOCHEMICAL RESULTS

pH

In all the samples collected from the various sites, pH values were higher than typical for groundwater in crystalline rocks (Fig. 4a). The highest pH values were found in groundwater from pipes A4, B30, and C14. The overall average pH for all samples was 9.54. The highest pH values were in the range of 12.4 at pipe A4. These elevated pH values are consistent with the hydration of ultramafic minerals (Clark and Fritz, 1997) and the formation of hydroxide alkalinity, CH_4 (methane), and H_2 (Deines and Langmuir, 1974). These reactions are expressed as equation 3 (Sherwood Lollar et al., 1993):

$$5Mg_2SiO_4 + Fe_2SiO_4 + 9H_2O = \quad (3)$$

olivine

$$3Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + 2Fe(OH)_2$$

serpentine ferrous hydroxide

Hydroxide alkalinity tests will be carried out at a later date. It is theorized that hydroxide alkalinity will be an important component of total alkalinity for groundwater with the highest pH values.

Oxidation-reduction potential

The oxidation-reduction potential or Eh of a water sample is a quantitative measure of the energy of oxidation in the system. For the most part, the Eh values for groundwater from the five kimberlite pipes are negative (Fig. 4b), indicating that the rocks are hydrating. Most samples fall within the range of being reducing basic water (Fetter, 2001; Fig. 5). Groundwater

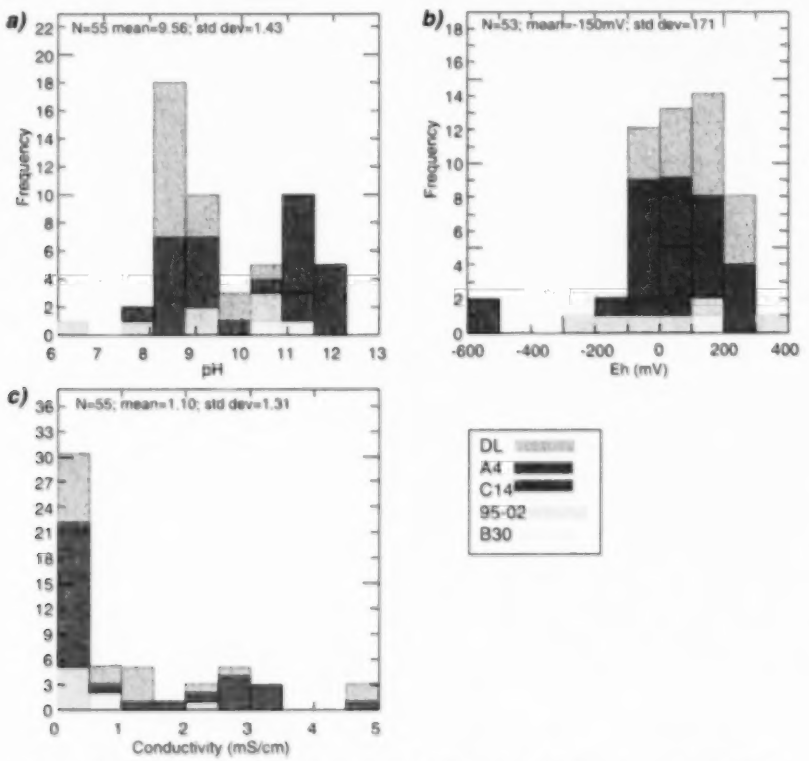


Figure 4. *Results for groundwater sampled at the five kimberlite pipes.* ***a)*** *pH;* ***b)*** *Eh;* ***c)*** *electrical conductivity.*

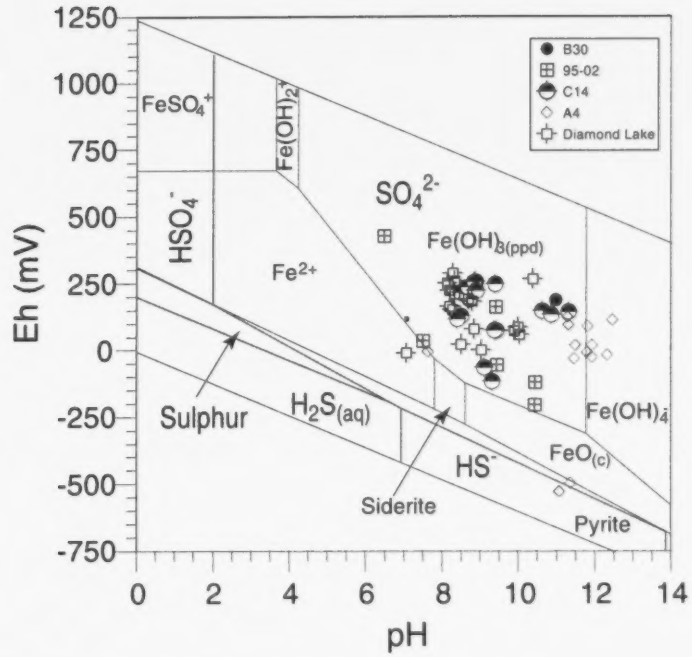


Figure 5.

Iron and sulphur stability fields and composition of kimberlite groundwater samples.

from kimberlite A4, which had the highest pH values and appeared to contain the most gas, yielded the lowest Eh values (as low as -536 mV). The Eh has a broad range of values from 425 to -536 mV. A correction of 230 mV was calculated for the Eh because of the difference between the platinum electrode used in the Hydrolab Corporation Quanta Microprobe and the standard hydrogen electrode. The iron and sulphur solubility fields in Figure 5 show that most waters are stable in the $Fe(OH)_3$ and sulphate fields. However, many of the A4 samples are more reduced and are stable at $Fe(OH)_4$.

Dissolved oxygen

Generally, most O_2 is formed by biogenic processes and if the dissolved oxygen levels in water drop below 4.0 mg/L, aquatic life is put under stress. The dissolved oxygen ranges from 0.38 to 5.43 mg/L in groundwater samples, suggesting that there is limited biological activity in many samples. Other higher values were recorded in our samples; however, these samples were taken from surface streams or from well tap water.

Electrical conductivity

The electrical conductivity of a water sample gives a rough indication of its salinity. Most samples have low conductivities (0.041–4.61 mS/cm; Fig. 4c). The most elevated conductivities were observed at pipes A4, DL, and 95-02 and likely represent enhanced water–rock reactions and/or mixing with deeper saline waters. Refinement of our interpretation will require a determination of major- and trace-element concentrations (data pending).

Pump-test recoveries

Simple pump tests were done on selected diamond-drill holes in order to get a quantitative idea of the porosity and groundwater flow in kimberlite pipes A4, C14, and 95-2. Recovery rates were generally rapid for those holes that were not blocked at the till–kimberlite contact, but much slower for holes that were blocked at the contact. All pump tests were carried out using the Grundfos electric pump set at 300 Hz (approximately 19 L/minute). Due to the high permeability and porosity of kimberlite material, apparently high flow rates were observed at all depths in all the holes sampled, and not just where fractures were located. The packer data and the pump-test data had suggested such results.

DISCUSSION AND CONCLUSION

The groundwater sampled from kimberlite pipes in northeastern Ontario is unusual with respect to pH and Eh. The information provided in this paper is preliminary and is based strictly on field results. However, some very interesting correlations were noted and processes inferred such as serpentinization and the hydration of ultramafic minerals.

The extremely high pH values measured in various samples are among the most interesting field results achieved. A maximum pH of 12.45 came from a slug collected at 65 m depth in borehole A at site A4. Drillholes in pipes A4, B30, and C14 contain groundwater with very high pH. The Diamond Lake and 95-02 pipes had relatively low pH values compared with the other three pipes. However, some groundwater samples gave unusually high pH values. The process hypothesized to raise the pH to such levels is the hydration of

ultramafic rock to produce hydroxide alkalinity (equation 3). Furthermore, some samples contained large volumes of gas. This gas could also be related to the process as some CO_2(aq) becomes incorporated into the system leading to the formation of CH_4 and H_2 (equation 4):

$$\text{olivine} + H_2O + C\ (\text{or } CO_2) = \quad (4)$$
$$\text{magnetite} + \text{serpentine} + CH_4 + \text{brucite} + H_2$$

(Sherwood Lollar et al., 1993)

These assumptions are reinforced by the Eh versus pH plot (Fig. 5), which suggests that the water may contain ferric hydroxide and other reducing species.

The hydration of olivine to form serpentine may also play a role in the permeability noted for all the kimberlite pipes. As the olivine hydrates, it gains mass and occupies up to 40% more volume (O'Hanley, 1992; Berndt et al., 1997; Schroeder et al., 2002). This would create a very friable kimberlite with numerous fractures, which could explain the rapid movement of groundwater through the kimberlite.

Future investigations

A number of analyses are underway for this study of groundwater in kimberlite. Analyses of major- and trace-element concentrations by ICP-OES and ICP-MS are underway at the University of Texas at Dallas. In addition, samples are being analyzed at the University of Ottawa for $\delta^{18}O$ and $\delta^{13}C$. Samples will be submitted for $\delta^{34}S$ analysis on sulphate and sulphide precipitation after X-ray diffraction analysis has been done on the filtrates to determine which samples contain sulphates or sulphides. Field results have shown the pH of kimberlite water to be high. By combining and correlating these data, future investigations may lead to the discovery of a new method for the exploration of kimberlite in northeastern Ontario.

From the data mentioned above, we hope to develop a theory of how kimberlite exploration can benefit from the use of groundwater geochemistry. Kimberlite is generally considered to be anomalous compared with surrounding rocks. It stands to reason that the groundwater will also be anomalous, with differences in major and trace elements, stable and radiogenic isotopes, and other processes that may be occurring.

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